

A STUDY OF THE DIFFUSION OF ELECTROLYTES
IN GELS

DISSERTATION

SUBMITTED TO THE BOARD OF UNIVERSITY STUDIES OF
THE JOHNS HOPKINS UNIVERSITY IN CONFORMITY
WITH REQUIREMENTS FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY

BY
B. WILSON ALLAN

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B. W. ALLAN

INTRODUCTION

The purpose of this paper is to give quantitative methods for the preparation of impregnated gels of silica, and to explain the anomalous effect of high acid concentration on the washing of such gels. The first portion of the paper deals with the preparation of impregnated gels; the second with the measurements of the diffusion rates of acid and salts in silica gel. The results of the diffusion measurements give an explanation of the behavior of the impregnated gels during dialysis.

EXPERIMENTAL I

Analyses of material

In the preparation of silica gels, it is important to know the concentration of the sodium oxide and of the silicon dioxide, and the ratio of these two in the water glass in order to duplicate the preparations. This information is often absent from papers dealing with the formation of such gels. The analysis of the water glass used in our experiments is as follows: NaOH = 3.56 molar; SiO₂ = 6.67 molar; ratio SiO₂ to Na₂O = 3.75.

Preparation of the gels

The method used for the formation of the gels impregnated with heavy metal salts is similar to that of Klosky and Patrick (1). A measured volume of a salt of known concentration was added to a definite amount of 10 normal hydrochloric acid solution. Various volumes of standard sodium silicate solution were then added to this salt-acid mixture. The combinations employed are shown in table 1.

General method for preparation of impregnated gels of silica

As the presence of the salt has but little effect on the sol-gel transformation, a good gel containing any of the above salts may be obtained in the

following manner. To 30 cc. of 10 *N* hydrochloric acid and 10 cc. of any of the salts used above, add with constant stirring 100 cc. of 1 per cent sodium silicate solution. The rigidity of the gels may be increased by using a more concentrated solution of water glass. These gels should then be washed until acid-free.

Behavior of the gels on washing

After the impregnated gels were successfully prepared, it was decided to determine quantitatively the loss of heavy metal ion during dialysis. Two

TABLE 1
Preparation of gels impregnated with heavy metal salts

NO.	SALT SOLUTION		HYDRO- CHLORIC ACID 10 <i>N</i>	SODIUM SILICATE 1 PER CENT	REMARKS
	Concentration	Volume added			
Iron gel					
		cc.	cc.	cc.	
1	0.1930 g.	5.0	2.5	100	Clear sol; no gel in two weeks
2	FeCl ₃	5.0	3.0	100	Clear sol; no gel in two weeks
3	per cc.	5.0	6.0	100	Clear sol; gel in one week
4		5.0	4.5	25	Clear sol; perfect gel in two hours
Copper gel					
1	0.2438 g.	5.0	5.0	100	Clear sol; no gel in one week
2	CuCl ₂	5.0	3.0	100	Precipitate
3	per cc.	5.0	5.0	70	Clear sol; soft gel in one week
4		5.0	5.0	30	Clear sol; gel in two hours
Manganese gel					
1	0.2148 g.	5.0	4.0	100	Clear sol; no gel in one week
2	MnCl ₂	5.0	5.0	100	Clear sol; no gel in one week
3	per cc.	5.0	5.0	90	Clear sol; gel in one week
4		5.0	5.0	30	Clear sol; gel in three hours

gels impregnated with ferric chloride were prepared. One contained a small amount of acid, the other a large amount. Two gels containing copper chloride were prepared in a similar manner. These gels were carefully analyzed before and after sixty hours of dialysis. The results are given briefly in table 2.

Two important facts were obtained from these analyses. Salts which are easily hydrolyzed are retained more strongly than those which are not, and salts are held more tenaciously by gels which contain a large excess of acid.

EXPERIMENTAL II

It is obvious that experiments like those described above are laborious and time-consuming; therefore it was desirable to attack the problem in another manner. Plans were now undertaken to measure the rate of diffusion of salts and acid through pure silica gel. However, none of the orthodox methods for measuring diffusion rates is applicable to silicic acid gel, owing to its shrinkage during syneresis and to its lack of adhesion to glass.

Finally it was decided to prepare permanent discs of silicic acid, and to measure diffusion through them. A mold was made from which thirty-six discs, 2.60 cm. in diameter and 1.90 cm. in thickness, could be made at once. These discs were made by preparing a sol of silicic acid which was then poured into the mold and allowed to set until gelation had occurred.

TABLE 2
Behavior of the gels on washing

GEL	SAMPLE	EXCESS ACID PER 100 CC. HYDROGEL	RATIO $\frac{\text{MOLES SiO}_2}{\text{MOLES Fe}}$	RATIO $\frac{\text{MOLES SiO}_2}{\text{MOLES Cu}}$
		<i>moles</i>		
Iron	Original gel	0.0173	6.94:1	
	Washed gel	0.0000	17.35:1	
	Original gel	0.4025	6.94:1	
	Washed gel	0.0000	16.69:1	
Copper	Original gel	0.0173		6.31:1
	Washed gel	0.0000		247.00:1
	Original gel	0.4025		6.31:1
	Washed gel	0.0000		151.62:1

They were then removed, dialyzed, and allowed to dry in the air several days. Of course the discs shrunk on drying. When they had decreased to a definite size, they were replaced in water. However after the gel discs had lost such a large amount of water, it was impossible to replace them in water without their cracking to pieces. This was due to surface strains brought about by the unequal absorption of water. By preparing a gel of low acid content this difficulty was overcome. The properties of this gel were superior to any of those previously prepared. The discs could be dried readily without breakage. A stream of water-laden air was passed over them in order to resaturate them gradually. After this treatment they could be replaced in water without any danger of breakage. On drying, all the discs did not shrink to the same size. Since only six discs were needed these could be selected with ease from the lot.

Figure 1 shows the apparatus in which the discs were employed. A series of such apparatus was arranged in a large air-bath thermostat which

was kept at a constant temperature of 32.50°C . A 20-liter aspirator bottle on the top of the thermostat acted as a distilled water reservoir. This was connected by glass tubing to a smaller aspirator bottle (2-liter) inside the thermostat. The small reservoir was so constructed that the water drawn from it was always under a constant pressure and temperature. A large tube (1.5 cm. in diameter) from which side arms protruded carried water from the small reservoir to each of the diffusion cells. These side tubes

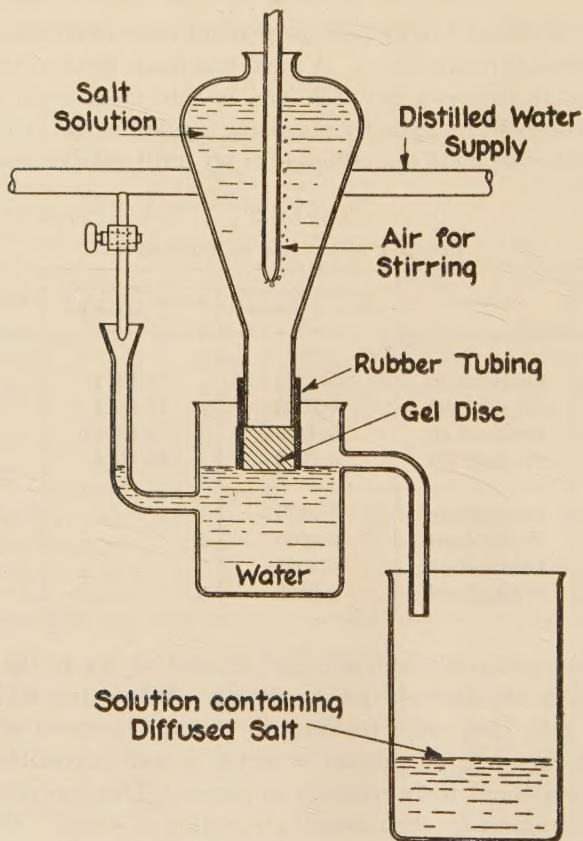


FIG. 1. APPARATUS USED IN MAKING THE MEASUREMENTS

entered the inlet tube of the cell. By means of stopcocks the flow of distilled water through these cells could be regulated. The rubber tubing in which the discs were held was attached to the reservoirs which were used to hold the salt solution. These salt reservoirs could easily be adjusted so that the face of the disc came in contact with the distilled water which flowed through the cell. After the salt reservoirs had been charged, the flow of water through the cells was regulated. The salt solutions were

stirred by bubbling air through them. This air had previously been saturated with moisture to prevent evaporation of the solvent from the salt solutions. Preliminary runs proved to be entirely satisfactory.

Measurements

The reservoirs were charged with their salt solution and the apparatus was adjusted and allowed to come to equilibrium. That is, diffusion was allowed to take place until the amount of solute passing through these discs per unit of time was constant. After this so-called "steady state"

TABLE 3
Results of the first run

NO.	SALT USED	ACID USED	CONCENTRATION OF SALT	CONCENTRATION OF ACID	TIME OF RUN	NaOH	AgNO ₃	NaOH IN TERMS OF AgNO ₃	GRAM-EQUIVALENT OF SALT DIFFUSED $\times 10^{-4}$
			<i>N</i>	<i>N</i>	<i>hours</i>	<i>cc.</i>			
1	LiCl	None	0.90	0	24	0	3.60		1.796
2	NaCl	None	0.90	0	24	0	6.40		3.193
3	KCl	None	0.90	0	24	0	8.95		4.470
4	LiCl	HCl	0.90	1.15	24	10.30	19.95	18.45	0.749
5	NaCl	HCl	0.90	1.15	24	12.80	25.50	22.95	1.273
6	KCl	HCl	0.90	1.15	24	13.30	27.55	23.80	1.872

TABLE 4
Average values of three runs

NO.	GRAM-EQUIVALENT OF SALT DIFFUSED $\times 10^{-4}$	DIFFUSION COEFFICIENT $\times 10^{-6}$
1	1.788	1.92
2	3.202	3.43
3	4.390	4.69
4	0.736	0.79
5	1.313	1.41
6	1.948	2.08

was reached, the liquid was removed from the cells, which were then thoroughly rinsed with distilled water. The flow of water through these cells was adjusted to the rate of 20 cc. per hour. Clean 800-cc. beakers were placed under each cell to catch the solution which flowed out of them. The thermostat was closed and the time recorded. After a definite time, approximately twenty-four hours, the run was discontinued. The solutions in the cells were removed and put in the beakers which had been placed under them. The cells were flushed out and this solution was added to that already in the beakers.

The salts used in these first measurements were lithium, sodium, and potassium chlorides; the acid was hydrochloric acid. The amount of diffusion was measured by analyzing the amount of salt and acid which came through the disc per unit of time. The amount of salt was determined by the method of Mohr, assuming that the concentration of the chloride ion gave a measure of the amount of salt present. Of course, in those experiments where both acid and salt were used, the concentration of the hydrochloric acid was first determined, then the total chloride con-

TABLE 5

The effect of different salts on the rate of diffusion of hydrochloric acid

NO.	SALT	CONCENTRATION	HCl (M)	NaOH (AVERAGE OF 3 RUNS)	DIFFUSION COEF- FICIENT (AVERAGE OF 3 RUNS)
		<i>molar</i>			
1	None	0	1.15	11.23	8.61×10^{-6}
2	CuCl ₂	0.3165	1.15	12.18	9.33×10^{-6}
3	FeCl ₃	0.2782	1.15	11.48	8.81×10^{-6}
4	LiCl	0.9000	1.15	16.03	12.21×10^{-6}
5	NaCl	0.9000	1.15	16.80	12.78×10^{-6}
6	KCl	0.9000	1.15	16.15	12.38×10^{-6}

TABLE 6

The effect of salts on the rate of diffusion of hydrochloric acid

NO.	SALT	CONCENTRATION	HCl (M)	NaOH (AVERAGE OF 3 RUNS)	AVERAGE DIFFUSION COEFFICIENT
		<i>molar</i>			
1	None	0	1.150	11.01	8.43×10^{-6}
2	CuCl ₂	0.6335	1.150	13.97	10.71×10^{-6}
3	FeCl ₃	0.5564	1.150	11.93	9.15×10^{-6}
4	LiCl	1.800	1.150	19.90	15.24×10^{-6}
5	NaCl	1.800	1.150	20.98	16.29×10^{-6}
6	KCl	1.800	1.150	20.02	15.37×10^{-6}

centration. Obviously, the difference gave the amount of salt. Since the end points in these titrations are hard to observe, all the solutions were concentrated to a small volume and actual titrations were done in artificial illumination. Also a blank was run before each series of analyses. The results of the experiments are given in tables 3 and 4.

The discs employed had the following dimensions: diameter, 1.18 cm.; thickness, 0.91 cm.; area of face, 1.094 cm.² The temperature of the thermostat was 32.50°C. Three such series of runs were made. The results in table 4 are average values of three runs.

It is seen from the results given in tables 3 and 4 that the order of the

diffusion coefficient is as follows: $K > Na > Li$. It is also shown that the diffusion coefficients of the salts are greatly affected by the presence of the acid. In each case the diffusion rate of each salt is diminished by the presence of acid.

Runs were now made to ascertain the effect of different salts on the rate of diffusion of hydrochloric acid. The discs employed had the following dimensions: diameter, 1.16 cm.; thickness, 0.90 cm.; area of face, 1.058 cm.² The time of each run was 24 hours. The results are given in table 5.

The concentrations of the salts were increased. The time of each run was 24 hours. The results are shown in table 6.

Table 7 gives the results obtained on increasing the concentration of the ferric and cupric chlorides.

The results of these experiments are plainly visible. The diffusion rate of the hydrochloric acid was increased by the presence of salts.

TABLE 7

The effect of salts on the rate of diffusion of hydrochloric acid

NO.	SALT	CONCENTRATION	HCl (N)	NaOH (AVERAGE OF 3 RUNS)	AVERAGE DIFFUSION COEFFICIENT
		<i>molar</i>			
1	None	0	1.150	11.10	8.52×10^{-6}
2	CuCl ₂	1.00	1.150	16.98	13.00×10^{-6}
3	FeCl ₃	1.00	1.150	14.92	11.43×10^{-6}

DISCUSSION

According to the Nernst theory of diffusion, which leads to the elementary explanation of the liquid potential, a mobile ion should increase the rate of diffusion of a more slowly moving oppositely charged ion. Furthermore, in the case of mixed electrolytes the more mobile ion will be retarded by the other ions, which in turn will experience an increase in mobility. This simple theory has been found to be in agreement with much experimental fact when dealing with ordinary diffusion phenomena. However, in the case of diffusion from a solution through a rigid gel structure, the above explanation no longer holds. Our washing of impregnated gels showed a marked retardation of the diffusion of the salt in the presence of acid, while our diffusion experiments through silica gel discs not only definitely proved the same point, but we were also able to show that the diffusion of the acid was speeded up in the presence of salt. These facts are in conflict with the Nernst theory; incidentally, Nernst never applied his ideas to systems such as used in this study.

One of the authors of this paper has recently developed a comprehensive theory which promises a satisfactory explanation of all the experi-

mental findings. Inasmuch as the development of the theory involves the discussion of much unpublished experimental work, it is thought inadvisable to attempt the argument at this time. Suffice it to say that it centers around an electrokinetic potential at the gel-solution interface.

SUMMARY

1. Quantitative methods have been worked out for the preparation of impregnated gels of silicic acid.
2. The anomalous effect of acid on the washing of such gels has been observed and an explanation has been advanced to account for the behavior.
3. Methods of preparing discs of silica gel, which permit the drying of such discs without shattering, have been discovered.
4. The diffusion of salts and acids has been studied in hydrated silica gel.

REFERENCE

- (1) KLOSKEY, SIMON: Dissertation, Johns Hopkins University, 1921.

BIOGRAPHY

The author of this dissertation was born in Baltimore, Maryland on February 10, 1907. He received his education in the Baltimore elementary schools and The Baltimore City College. He entered The Johns Hopkins University in 1926. In 1928, he was admitted to The School of Higher Studies of the Faculty of Philosophy under the New Plan as a graduate student in chemistry.

